AN ¹⁸O-TRACER STUDY ON THE TIO₂-SENSITIZED PHOTOOXIDATION OF AROMATIC COMPOUNDS

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 ${\rm TiO}_2$ -sensitized photooxidation of benzenes has been studied to disclose the origin of the ring hydroxylating species. An 18 O-tracer study using 18 O₂ gas revealed that the hydroxyl group of phenols comes essentially from molecular oxygen at higher pH region. At lower pH, however, the oxygen atom in phenols originates mostly from solvent water. These findings are compatible with two different mechanisms proposed by Osa et al. and Tokumaru et al.; that is, the major pathway changes with pH.

Much attention has been focused on photocatalytic reactions using semiconductors.¹⁾ Aerobic irradiation of powdered TiO_2 suspended in a mixture of aromatic compound and water has been shown to induce ring hydroxylation as well as side chain oxidation. The photocatalytic hydroxylation of toluene to give cresols was named by Fujihira and Osa et al.²⁾ "Photo-Fenton Type Reaction" on the basis of its parallelism with the Fenton reaction³⁾ in involving hydroxyl radical (HO·) formed via the reduction of oxygen by electron in the conduction band of TiO_2 (Eq. 1). Tokumaru and coworkers⁴⁾ have demonstrated that HO· is formed via the oxidation of water by positive hole (h⁺) of ^{*}TiO₂ with concurrent removal of the electron by molecular oxygen. Relevant and/or proposed sequences for the photooxidation of toluene are as follows.¹⁻⁴

$$\operatorname{TiO}_{2} \xrightarrow{h\nu} h^{+} + e^{-}$$
(1)

$$o_2 + e^- \rightarrow o_2^- \cdot \rightarrow H_2 o_2^- \rightarrow HO \cdot$$
 (2)

 $H_{2}O + h^{+} \longrightarrow HO \cdot + H^{+}$ (3a)

$$HO^{-} + h^{+} \longrightarrow HO^{-}$$
 (3b)

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Ho. +
$$(1)^{\text{CH}_3} \xrightarrow{\text{HO}}_{\text{H}} (1)^{\text{CH}_3} \xrightarrow{\text{oxidn.}}_{\text{CH}_3} (4)$$

$$\bigcirc -CH_3 + h^+ \longrightarrow \textcircled{+} -CH_3 \rightarrow \bigcirc -CH_2 \cdot + H^+ \tag{5}$$

$$\bigcirc -CH_2 \cdot \xrightarrow{O_2} \bigcirc -CH_2 OO \cdot \longrightarrow \bigcirc -CHO + \bigcirc -CH_2 OH$$
(6)
$$\xrightarrow{\text{dimerzn.}} \bigcirc -CH_2 CH_2 - \bigcirc$$
(7)

One of the remaining questions is which of the two processes, Eq. 2 or Eq. 3, should be a major pathway for the source of the hydroxyl radical. In the course of

our study on metallic ion-sensitized photooxidation of aromatic compounds,⁵⁾ we became interested in the question. We wish to report here an¹⁸O-tracer study disclosing that the origin of HO· changes with pH, i.e., from the reduction of oxygen (Eq. 2) at higher pH to the hole oxidation of water (Eq. 3) at lower pH.

A mixture of toluene (2.8 m mol) and TiO₂ (0.13 mmol) in alkaline water (3.5 ml, pH 12) was degassed by three freeze-thawcycles and sealed under appropri-





ate pressure of oxygen gas. The irradiation was carried out for 3 h with a 500 W Philips high pressure mercury arc lamp filtered by a Pyrex glass. Figure 1 shows

Table 1. ¹⁸O Content in the Photoproducts of the TiO_2 -Sensitized Photooxidation under ¹⁸O₂ - O₂ (28:72)^{a)}

R in	18 ₀ Content of Photoproduct (%)		
R-	О-сн ₂ он	О-сно	R-OH
CH ₃	92 ± 4	1 ± 2	78 ± 7
Н	-	-	70 ± 8

a) A mixture of 0.3 ml of toluene or benzene and 10 mg of TiO₂ in aqueous NaOH (pH 12) was degassed, sealed under 300 mmHg of oxygen gas (28% $^{18}O_2$) and irradiated with a Pyrex-filtered light (Philips SP lamp, 500 W).

that the photooxidation is affected by oxygen pressure, and the product distribution at $P_{O_2} = 1$ atm is similar to the reported one.²) It is interesting to note that the formation of bibenzyl decreases and that of cresols increases at higher oxygen pressure.

In order to search for the origin of the oxygen atom in the photoproducts, the photooxidation of toluene with aqueous TiO_2 was carried out in the presence of $^{18}\text{O}_2$ gas. The results in Table 1



implies that the oxygen atom of cresols and benzyl alcohol originates mainly from oxygen gas, but not from water. A very low content of 18 O in benzaldehyde may be due to facile exchange of the oxygen atom with solvent water. Likewise, molecular oxygen is responsible for the formation of phenol from benzene. The results in Fig. 1 and Table 1 suggest that oxygen gas is effectively converted to the hydroxyl radical as a result of electron acceptance in alkaline solution (pH 12) (Eq. 2).

Figure 2 shows a pH dependence on 18 O content of phenol for the TiO₂-sensitized photooxidation of benzene in the presence of ${}^{18}O_2$ gas.⁶) Redox potential consideration^{7,8} suggests that the h⁺ oxidation of water (Eq. 3) is independent of pH, while the e⁻ reduction of O₂ (Eq. 2) decreases at lower pH because of competitive electron trap by H⁺ to give hydrogen. Therefore, HO· radical should be mainly formed by the reduction of O₂ (Eq. 2) at higher pH, and via the oxidation of water (Eq. 3) at lower pH. In fact, Fig. 2 indicates that the oxygen source for phenol changes steadily from molecular oxygen to solvent water with decreasing pH.

Side-chain oxidation products from toluene, e.g., benzyl alcohol and benzaldehyde, are derived from the addition of oxygen to benzyl radical.^{4b)} Following deuterium labeling experiments support that the benzyl radical is produced via the one-electron oxidation (Eq. 5) rather than the direct hydrogen atom abstraction by HO.. When the deuterium contents in bibenzyl from the photolysis of toluene- α -d₁ were measured, the kinetic isotpe effect for the formation of benzyl radical was estimated to be $k_{\rm H}/k_{\rm D}$ = 2.93 ± 0.07. This value is comparable to those reported as one-electron oxidation; e.g., 2.91 ± 0.09 for the photooxidation with Fe³⁺ and 3.09 ± 0.09 with *p*-dicyanobenzene,⁵⁾ and smaller than those for hydrogen radical abstraction, e.g., 4.9 for bromine radical^{3b)} and 5.12 ± 0.07 for butoxy radical.⁵⁾

In summary, the present 18 O tracer study demonstrates that the hydroxylation of aromatic rings proceeds through two different reaction pathways depending on pH. At higher pH region benzenes are attacked mainly by the hydroxyl radical formed by one-electron reduction of molecular oxygen with the excited TiO₂. On the contrary, at lower pH region benzenes are attacked with the hydroxyl radical formed by the h⁺ oxidation of water. The resulting hydroxycyclohexadienyl radicals (1) lead to phenols or side-chain oxidation products.

References

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